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### (54) GAS PHASE CATALYTIC FLUORINATION OF HALOGENATED HYDROCARBON

(57)Abstract:

PURPOSE: To obtain a compd. useful as a cooling medium, a blowing agent or the like by efficiently performing the gas phase catalytic fluorination of halogenated hydrocarbon by hydrofluoric acid by using a mixed catalyst based on chromium and vanadium derivatives and characterized by that these two elements are in the oxidation state III.

CONSTITUTION: A halogenated hydrocarbon is subjected to gas phase catalytic fluorination by hydrofluoric acid by using a mixed Cr-V catalyst wherein a V/Cr atomic ratio is 0.1-3.5, pref., 0.15-3 and 90% or more of Cr and V is in the oxidation state III. The catalyst is pref. bonded to a carrier such as aluminum trifluoride or the like. It is pref. to fluorinating 1-chloro-2,2,2-trifluoroethane by using gas phase catalytic fluorination to obtain 1,1,1,2-tetrafluoroethane.

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### LEGAL STATUS

[Date of request for examination]

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## DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] this invention makes the theme use of the catalyst which made chromium and vanadium the base material in more detail about manufacture of the fluorine carbonizing-ized hydrogen by forming a halogenated hydrocarbon into a gaseous-phase contact fluorine using a hydrofluoric acid.

[0002]

[Description of the Prior Art] Chlorofluorocarbon (CFCs) Composition of a fluoridation hydronalium haloalkane was especially filled with the intensive research which led to the substitute. The heterogeneous-system gaseous-phase contact fluoridation which uses a hydrofluoric acid can perform some stages of this composition.

[0003] Since it is a complicated compound and reactivity is more chemically [ than CFCs ] higher than CFCs especially mostly, these hydronalium haloalkanes need development of a more nearly alternative catalyst for those composition in activity more.

[0004] Very many metallic compounds (for example, chromium, cobalt, nickel, manganese, magnesium, vanadium, copper, etc.) show the catalyst effect in these fluoridation reactions. The catalyst proposed by reference is either a bulk catalyst or a support catalyst, and carbon, an alumina (converted into  $AlF_3$  in fluoridation trailer), or 3 aluminum fluoride is usually mainly used as support.

[0005] Combined use of chromium and vanadium is known for manufacture of an oxidation catalyst. For example, the claim of the bulk catalyst which made the base material the oxide of the vanadium and chromium which are used for the oxidization to the carboxylic acid of aliphatic hydrocarbon is carried out to patent EP 002 and 682.

[0006] In the field of the fluoridation, there is almost no reference which mentioned use of the vanadium in a fluoridation catalyst.

[0007] F134a by the formation of a gaseous-phase fluorine of the halogenation olefin on the catalyst which made the base material the chromium and transition metals of 6 \*\* supported to the alumina about this at the patent EP 295,885 (1, 1, 1, 2-tetrafluoro ethane) Composition is indicated. Especially a desirable thing is titanium as transition metals. The example is not given although reference is made about vanadium. ; which leaves a solid-state alumina and performs sinking in by the solution of a chrome oxide (VI) and a transition-metals salt -- in the last of the manufacture, chromium is still in VI state and other metals are in the state (in the case of titanium oxidation state IV) where it oxidized

[0008] Furthermore, the method of preparation of the fluoridation olefin by transformer halogenation using the catalyst which makes a base material the chrome oxide or aluminum oxide combined with the compound of other elements which contain vanadium in patent EP 203,807 is indicated. An example is not given about the mixed catalyst which makes the vanadium a base material, and the basic reaction is not a fluoridation reaction included in this invention.

[0009] Moreover, vanadium is used also for liquid phase fluorine-ization. The fluoridation of the haloalkane using the fluoride of transition metals like 5 vanadium fluoride is indicated by the patent EP 503,792.

[0010] the same -- Bardin et al. [J.Flour.Chem.(1990) 49(3) 385-400] \*\*\*\* -- the liquid phase fluoridation (addition of two fluorine atoms) of an olefin is indicated The fluoridation agent used is VF<sub>5</sub> compounded by carrying out the direct fluoridation of the vanadium metal using a fluorine.

[0011]

[Problem(s) to be Solved by the Invention] The purpose of this invention is to offer the method of carrying out the gaseous-phase contact fluoridation of the halogenated hydrocarbon by the hydrofluoric acid using the catalyst which made chromium and vanadium the base material.

[0012]

[Means for Solving the Problem] It sets to the gaseous-phase fluoridation of the saturation using HF, or an olefin system halogenated hydrocarbon, and vanadium and chromium are mainly an oxidation state III. Use of the existing mixed Cr-V catalyst did not yet know that the catalyst performance superior to the catalyst performance which is chromium independent or is obtained by the vanadium independent is obtained. Furthermore, III It is volatile vanadium, while loss of vanadium can be reduced considerably, if the vanadium and chromium in a state are used. (V) Generation of an oxy-fluoride or a fluoride is avoidable. Therefore, oxidation state III While the existing mixed Cr-V phase can improve a catalyst performance, it can restrict loss of active species.

[0013] Therefore, in the method of carrying out the gaseous-phase contact fluoridation of the halogenated hydrocarbon by the hydrofluoric acid, the mixed catalyst which makes chromium and vanadium a base material is used for the theme of this invention, and these two elements are mainly oxidation states III. It is the method characterized by being.

[0014] " -- mainly -- " -- chromium and at least 80% of a vanadium element (preferably 90% or more) -- oxidation state III The meaning of being is meant.

[0015] The catalyst by this invention may be a support catalyst even if it is a bulk catalyst, and the ranges of a V/Cr atomic ratio may be 0.05-5. The atomic ratio 0.1-3.5 Between is convenient and is between 0.15-3 preferably.

[0016] The catalyst used in this invention can be prepared from chromium and a vanadium precursor using the method well-known in itself for acquiring a bulk catalyst or a support catalyst.

[0017] It is usable no matter it may be what other chromium compounds as a chromium precursor if the uniform mixture of chromium and vanadium can be manufactured in solid phase, although the oxide, the hydroxide, the halogenide, the oxy-halogenide, the nitrate, the acetate, oxalate, and sulfate of chromium are mentioned. Precursors desirable to manufacture of a bulk catalyst are a chloride and an especially desirable chromium salt like a sulfate, acetate, and a nitrate. In manufacture of a support catalyst, it is a chromium chloride (III). Or it is desirable to use a chromic-acid anhydride (CrO<sub>3</sub>).

[0018] The vanadium precursor which can be used is not spread slightly. a chloride, acetylacetonate, an oxysalt ghost, and an oxy-sulfate mention -- having -- especially a desirable thing -- vanadium chloride (III) it is .

[0019] The method of preparation of the bulk catalyst according to this invention for example, although not necessarily limited is the above-mentioned chromium (III). And it is in the reduction of CrO<sub>3</sub> under the neutralization using the bases (a sodium hydroxide, aqueous ammonia, amine, etc.) of a vanadium compound, otherwise, existence of the above-mentioned vanadium compound. next, it dries, after washing the obtained precipitate or gel -- it calcinates at the temperature between 200 - 600 \*\*s

[0020] Moreover, the bulk catalyst by this invention can also be acquired by pyrolysis (200-450 \*\*) of the oxalate of the chromium settled in organic media (alcohol, the ether, chlorinated hydrocarbon, etc.), and vanadium.

[0021] Secondary forming of the final catalyst can be carried out to this contractor with any well-known technology (tablet-izing, extrusion, granulation, etc.). In order to raise the physicochemical property and catalyst property of an end product, you may add various additives to the preparation. For example, :(% of mass criteria to mass of final catalyst)- which can add the following additive In order to improve the mechanical behavior of a final catalyst, beforehand -- Powdered Cr<sub>2</sub>O<sub>3</sub> dried at 300 degrees C or Cr<sub>2</sub>O<sub>3</sub>.2H<sub>2</sub>O -- Or aluminum<sub>2</sub>O<sub>3</sub>, 2O<sub>2</sub> - 30% of xH(s), - In order to promote secondary forming by tablet-izing or extrusion, Graphite 0.1 - 5%, and/or polyvinyl alcohol 0.1 - 10%, - A flocculant like the

polyacrylate or polyacrylamide for promoting filtration of the cake collected after neutralization 0.1 - 20%.

[0022] The support which is used in the case of a support catalyst must suit with the medium containing HF. Support like metallic oxides, such as 3 aluminum fluoride, and an alumina, a magnesia, a zirconia, usually used is suitable. Since the fluoridation is generally carried out under HF atmosphere (exothermic reaction which produces water), when using this oxide, before these oxides sink in with chromium and a vanadium compound, it is desirable [ oxides ] mostly to expose them to fluoridation conditions. sinking [ which support requires ] in -- for example, the solution of  $\text{CrCl}_3$  and  $\text{VCl}_3$  -- or a reducing agent like two solution of the solution containing  $\text{CrO}_3$  and the solution containing  $\text{VCl}_3$  and a methanol can perform Moreover, support (carbon) may be contained as a reducing agent. the case of such a support catalyst -- all the contents of chromium and vanadium -- weight criteria 0.5 - 25% of range -- it may be 2 - 15% of range preferably

[0023] The mixed Cr-V catalyst by this invention is applicable to gaseous-phase fluorine-ization of the saturation which used HF, or an olefin system halogenated hydrocarbon. Especially those catalysts are suitable for fluorine-ization of the halogenated hydrocarbon from which the fluorine-ized compound of C1-C4 containing one or more hydrogen atoms is obtained as a result. As an example of a halogenated hydrocarbon used as a start raw material, although not necessarily limited It  $\text{CHCl}(\text{s})$  : which can mention the following compound --  $\text{CHCl}_3$ ,  $\text{CH}_2\text{Cl}_2$ , and  $\text{CCl}_2=$  --  $\text{CHCl}_2\text{-CClF}_2$ ,  $\text{CHCl}_2\text{-CF}_3$ ,  $\text{CHFCl-CF}_3$ ,  $\text{CH}_3\text{-CCl}_3$ ,  $\text{CH}_3\text{-CFCI}_2$ ,  $\text{CH}_3\text{-CF}_2\text{Cl}$ ,  $\text{CH}_2\text{ Cl-CF}_3$ ,  $\text{CH}_3\text{-CCl}_2\text{-CH}_3$ ,  $\text{CCl}_3\text{-CF}_2\text{-CH}_3$ ,  $\text{CCl}_3\text{-CF}_2\text{-CHCl}_2$ ,  $\text{CCl}_3\text{-CF}_2\text{-CH}_2\text{Cl}$ ,  $\text{CHCl}_2\text{-CHCl-CH}_3$ ,  $\text{CH}_2\text{ Cl-CHCl-CH}_3$ , and  $\text{CCl}_2=\text{CCl}_2$  ; Although the compound of this last does not contain hydrogen, if HF is added, a halogen hydrogenation compound will be produced as a result.

[0024] In order to make it act in the highest activity, it is necessary to process a catalyst by the hydrofluoric acid which is not diluted or was diluted with nitrogen. Although crystallization will become slow if vanadium exists, it is on a partial target by such activation. It may become temperature higher than 500 degrees C. It is low temperature about this processing in adding a diluent to HF by such a translation \*\*\*\*. (150-250 \*\*) Controlling the calorific value of the activation is recommended by making it start. On the other hand, when "the wave of calorific value" in a catalyst bed passes, it is the maximum at the last time of activation. Raising temperature gradually so that 350 - 450 \*\* may be reached is recommended.

[0025] When chromium and/or vanadium with a larger oxidation state than 3 are contained in the catalyst which is not activated by high concentration, in order to prevent great loss of the vanadium by generation of the volatile kind after activation, and/or chromium, it is good before this activation to perform a reduction stage (heat treatment between neutrality or 200in reducing atmosphere -400 \*\*).

[0026] the reaction by which the temperature of the fluoridation of an organic substance was examined - and it is completely clearly dependent on a desired resultant For example, when adding HF to a double bond, or when a fluorine replaces a chlorine atom partially, the work is made at the temperature between 50 - 350 \*\*s. When replacing all chlorine atoms, it is on a general target. The temperature between 300 - 500 \*\*s is required.

[0027] Moreover, contact time is also dependent on the examined product which is reacted and meant. In most cases, it is 3-100. In order to acquire the suitable compromise of; which it is during a second however the degree of inversion, and space time yield, it is convenient to make contact time into less than 30 seconds.

[0028] Moreover, the mole ratio of HF/organic compound is also related to the considered reaction. The mole ratio divides and is dependent on the stoichiometry of the reaction. Although it may change between 1/1 and 20/1 most cases, in order to obtain yield at the time of altitude, it is less than ten mostly again here.

[0029] A work pressure is 1-20 bars at absolute pressure. (0.1-20MPa) Between is desirable.

[0030] Depending on mechanical toughness, the catalyst by this invention can act in the fixed bed or the fluid bed. The catalyst from which activity fell is reproducible by becoming dirty by purging a catalyst with a compound with the capacity which oxidizes and converts the products (an organic substance,

corks, etc.) which adhered on the catalyst in an volatile product. The mixture (for example, air) containing oxygen or oxygen can suit this purpose perfect, and can recover the activity in early stages of the catalyst.

[0031] In order to secure reproduction of a catalyst, without producing oxidization of crystallization or vanadium of a catalyst, and chromium, performing this processing at the temperature which does not exceed 350 degree C is recommended. So, in order to hold the temperature of less than 350 degrees C, it is good that what (the oxygen of a low flow rate is diluted with inert gas at the time of a reproductive start) the flow rate of oxygen is controlled for restricts the calorific value by this "combustion."

[0032] in order [ moreover, ] to hold the activity of a catalyst -- O<sub>2</sub> / organic compound mole ratio 0.001 to 0.05 -- desirable -- A fluorine-ized reaction can also be performed under existence of the oxygen introduced so that it might become the range of 0.005-0.03. In this case, in order to avoid oxidization of vanadium and chromium, working at the temperature which does not exceed 400 degree C is recommended.

[0033]

[Example] Hereafter, although an example explains this invention, this invention is not limited to these.

[0034] Manufacture catalyst 1 chromium-nitrate 9 monohydrate Cr(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O 20g of a catalyst (0.05 mols) And vanadium-trichloride VCl<sub>3</sub> 1.57g (0.01 mols) Water It is 14N NH<sub>4</sub>OH 14ml about the solution after dissolving in 100ml. It uses and neutralizes and is pH 6.4. It adjusted. It filters, after washing the obtained gel with water, and it is in oven. It dried at 120 degrees C for 14 hours. Next, the powder obtained by doing in this way was calcinated at the bottom of nitrogen, and 350 degree C for 4 hours.

[0035] The solution which dissolved 32g of ammonium-oxalate 1 monohydrates, 1.15g of vanadium trichlorides, and 27g of chromium-nitrate 9 monohydrates in 75ml of water was prepared under 260 degrees C of catalysts, and stirring. Thus, ethanol after cooling the obtained transparent solution 375ml and ethylene glycol It poured quickly into 375ml mixture.

[0036] Next, mixed complex (NH<sub>4</sub>) [Cr<sub>x</sub>V<sub>1-x</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>] 3 obtained by doing in this way It decomposed by 350 \*\* among air, and the amorphous catalyst of the oxide of chromium and vanadium was manufactured.

[0037] VCl<sub>3</sub> of the amount of 32 times as many catalysts as this (2.3g) And more nearly little Cr(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (24g) It prepared by the same method as a catalyst 2 except having used it.

[0038] It is vanadium-trichloride-oxide VOCl<sub>3</sub> 1.73g (0.01 mols) instead of catalyst 4(example of comparison) VCl<sub>3</sub>. It prepared by the same method as a catalyst 1 except having used it.

[0039] VOCl<sub>3</sub> 1.73g is used instead of catalyst 5VCl<sub>3</sub>, and it is VV. VIII In order to return, it prepared by the same method as a catalyst 1 except using the mixture (N<sub>2</sub>/H<sub>2</sub> mole ratio : 95/5) of nitrogen and hydrogen, and performing baking.

[0040] 32g of catalyst 6 (example of comparison) ammonium-oxalate 1 monohydrates and VOCl<sub>3</sub> 13g were mixed at 60 degrees C under stirring in 75ml of water. Next, the oxalic acid complex obtained by doing in this way is decomposed by 350 \*\* among air, and it is a vanadium oxide (V). The catalyst was manufactured.

[0041] 30ml of support which contains an alumina for aluminum fluoride 27% 73% on weight criteria was put into catalyst 7 rotating evaporator. This support is a big surface area. (>180 m<sup>2</sup>/g) About the alumina which it has, they are the inside of the fluid bed, and abbreviation. It is obtained by the preceding paragraph story by borrowing and carrying out the fluoridation of the assistance of air and a hydrofluoric acid (the concentration of this acid in air is 5 - 10% at volume criteria) at 300 degrees C.

[0042] Moreover, methanol solution containing : (a) : 3.8 g-water : 9 g which also prepared two kinds of solution separately. - chromic-acid anhydride (CrO<sub>3</sub>) : 3.2 g-water : 3 Chromic-acid solution containing g (b) -3 vanadium chloride (VCl<sub>3</sub>) : 5 g-methanol [0043] Next, it introduced on support under stirring, having applied [ of two kinds of these solutions ] it for about 45 minutes with ambient temperature and atmospheric pressure. Subsequently, it is abbreviation in the nitrogen style in the fluid bed about a catalyst. It dried at 110 degrees C for 4 hours.

[0044] The solution which dissolved VCl<sub>3</sub> 5g in 11ml of water instead of the methanol solution of

catalyst 8(example of comparison)  $\text{VCl}_3$  was used, and chromium was prepared by the same method as a catalyst 7 except having not returned with a methanol.

[0045] About catalyst 9 support, it is chromium chloride (III) 6 monohydrate. It prepared by the same method as a catalyst 7 except having sunk in with 8.5g,  $\text{VCl}_3$  5g, and one kind of solution containing 14g of water.

[0046] They are  $\text{VOCl}_3$  5.4g and a methanol instead of the methanol solution of catalyst 10 $\text{VCl}_3$ . It prepared by the same method as a catalyst 7 except having used the solution containing 3.8g and 5g of water.

[0047] It prepared by the same method as a catalyst 7 except having used the solution which dissolved  $\text{VOCl}_3$  5.4g in 8g of water instead of the methanol solution of catalyst 11(example of comparison)  $\text{VCl}_3$ .

[0048] The chromic-acid solution and methanol which dissolved catalyst 12(example of comparison)  $\text{CrO}_3$  3.2g in 5g of water It prepared by the same method as a catalyst 7 except having used the methanol solution which dissolved 3.8g in 7g of water, and having not used vanadium.

[0049] It prepared by the same method as a catalyst 7 except having used the support which sank in with one kind of solution containing catalyst 13(example of comparison)  $\text{VCl}_3$  5g, 10g [ of water ], and methanol 2g, and having not used chromium.

[0050] F133a The performance and amorphous substance  $\text{Cr}_2\text{O}_3$  of the fluorine-ized catalysts 1-13 About the performance of a bulk catalyst (the following catalyst 14), it is 1-chloro after activation and in atmospheric pressure. - 2, 2, 2 - Truffe RUORO ethane (F133a) It examined in fluorine-izing.

[0051] It is F133a which the commercial elegance containing the water of a ultralow volume is used as a hydrofluoric acid, and is a start raw material. If carried out, the product of 99.9% of purity was used. As a reactor, it is 20-ml heated by the tubular furnace. The Inconel tube was used.

[0052] Activation of the catalyst using HF is 15-ml in this reactor. The sample was followed. The bottom of nitrogen (0.1mole/time), and after drying at 200 degree C for 2 hours, HF was gradually added at this temperature. HF flow rate after the peak of generation of heat passes It increases till 0.1mole/time, and, next, is temperature. It raised to 350 degrees C. The plateau of temperature was observed on these conditions for 10 hours.

[0053] The reactant was mixed, and it introduced into the reactor, after heating to reaction temperature in an Inconel preheater.

[0054] The resultant was washed with water (a hydro acid is removed), and after drying on  $\text{CaCl}_2$ , the vapor phase chromatography analyzed with in-line.

[0055] The main properties of an activation catalyst and the loss percentage of the vanadium under activation are shown in Table 1.

[0056] In Table 2 and 3, it is F133a. The operating condition of the fluoridation and the obtained result are summarized.

[0057]

[Table 1]

## 活性化触媒の特性

触媒No.	BET 表面積 ( $\text{m}^2/\text{g}$ )	元表分析 (重量%)				バッチ 損失 %
		Cr	V	Al	F	
バルク形						
1	43.4	45.9	7.1	0	19.7	7
2	50.5	47.6	2.4	0	35	7
3	52.4	42.2	6	0	31.2	9
4 (比較)	56.4	49.5	6.4	0	19.2	25
5	55.8	48.3	7.6	0	18.5	10
6 (比較)	32	0	48.1	0	24	測定せず
14 (比較)	110	54	0	0	21	
担持形						
7	51.6	4	3.8	26.6	60.6	5
8 (比較)	43	5.2	1.3	26.6	62.3	40
9	45.9	6.1	4.8	25.3	59.2	3
10	54.5	6.6	2.6	24.8	59.6	28
11 (比較)	47	7.1	1.4	26.8	61.9	53
12 (比較)	39.5	6.3	0	27.2	61.8	-
13 (比較)	36.3	0	4.3	27.7	62.6	3

[0058]

[Table 2]

350℃、大気圧でのF133aのF134aへのフッ素化 バルク触媒

試験	F1	F2	F3	F4	F5	F6	F7	F8	F9	F10	F11
<b>操作条件:</b>											
触媒 No.	1	1	1	2	3	4	5	14	14	14	6
HF/F133a モル比	4.5	4.1	4	5.2	4.2	4.1	4.2	3.9	4.2	3.8	3
O <sub>2</sub> /F133a モル比	0	0	0.005	0	0	0	0	0	0	0.005	0
接触時間 (秒)	4	2.1	0.5	3.6	4	3.9	3.8	4.2	3.9	0.6	3.5
触媒齢 (時間)	20	46	133	24	24	25	23	67	340	24	23
<b>結果:</b>											
F133aの全転化率 (%)	21.2	21.3	20.1	22.6	21.1	22.9	21.5	20.9	15.5	15.1	3
<b>選択度 (mol%):</b>											
- F134a (CF <sub>3</sub> CH <sub>2</sub> F)	97.1	97.5	93.3	97.4	97.4	95.8	95.9	95.7	97.1	92.3	34.8
- F1122 (CF <sub>3</sub> =CHCl)	0.9	0.9	1.6	0.9	0.7	1.3	1.4	1	1	1.1	4.6
- F120 系 (')	1.2	0.7	3.3	0.8	0.4	0.7	0.6	1	0.6	4.8	0.3
- F143a (CF <sub>3</sub> CH <sub>3</sub> )	0.5	0.6	0.2	0.2	0.8	0.9	0.7	1.4	0.3	0.3	59.6
- その他	0.3	0.3	1.4	0.7	0.7	1.3	1.4	0.9	1	1.5	0.7

・ 結合ヒドロペンタハロエタン類

[0059]

[Table 3]

350°C、大気圧でのF133aのF134aへのフッ素化 担持触媒

試験	F12	F13	F14	F15	F16	F17	F18	F19	F20	F21
操作条件:										
触媒 No.	7	7	8	9	9	10	12	12	12	13
H <sub>2</sub> /F133a モル比	4.5	4.1	4.1	4	4	4.1	3.8	3.9	4	4
O <sub>2</sub> /F133a モル比	0	0.005	0	0	0	0	0	0	0.005	0
接触時間 (秒)	4	0.5	4	3.9	4	3.9	4.1	4.2	0.5	4
触媒年齢 (時間)	20	24	43	24	250	24	24	151	23	19
結果:										
F133aの全転化率 (%)	19.3	15.2	21.8	20.5	20.1	20.9	20.7	15.2	12.3	3
選択度 (mol %):										
- F134a (CF <sub>3</sub> CH <sub>2</sub> F)	98.4	96.7	98.1	98.2	98.1	97.4	97.9	98	96.6	78.4
- F1122 (CF <sub>2</sub> =CHCl)	0.7	1	0.9	0.6	0.7	1.2	1.3	0.7	0.9	11.7
- F120 系 (*)	0.5	1.4	0.5	0.8	0.9	0.6	0.3	0.3	1.6	9.3
- F143a (CF <sub>3</sub> CH <sub>3</sub> )	0.4	0.5	0.5	0.4	0.3	0.3	0.4	0.3	0.6	0.3
- その他	0	0.4	0	0	0	0.5	0.1	0.7	0.3	0.3

・ 結合ヒドロペンタハロエタン類

[0060] the result which was alike and set as far as it is related with a bulk catalyst, and was obtained by examinations F1-F3 and F7 -- especially short contact time (examination F3) The obtained result to chrome oxide (III) Independent (examinations F8-F10) or vanadium oxide (V) Independent (examination F11) comparing -- mixed CrIII-VIII It turns out that it obtains that the activity of a catalyst is better and says. As for a manufacture method:sol-gel path (catalyst 1-examinations F1-F3) and an oxalate path (a catalyst 2 and 3-examinations F4 and F5), examinations F1-F5 show that what the catalyst performance resembles as a result is obtained.

[0061] When the precursor of the chromium which is in an oxidation state 3 when Table 1 is

investigated, and vanadium is used, a low is known in loss of the vanadium under activation of a catalyst (catalysts 1-3). If an oxidation state uses the precursor of larger vanadium than 3, unless reduction-baking will be performed before activation (catalyst 5), the loss which starts under activation becomes higher (catalyst 4).

[0062] Moreover, in the case of a support catalyst, it is examination F15. And F16 The obtained result to Cr<sub>2</sub>O<sub>3</sub> It compares with independent (examination F18 and F19), and is mixed CrIII-VIII. It turns out that the stability of a catalyst is better.

[0063] For example, AlF<sub>3</sub> Supported CrVI-VIII Although a mixed catalyst shows (a catalyst 8) and good activity (examination F14), loss of the vanadium in an activation stage is high. (40%) . These losses are chromium (VI) and vanadium (III). It is thought that it is based on the oxidation-reduction reaction of a between.

[0064]

[Effect of the Invention] The mixed Cr-V catalyst by this invention shows the catalyst performance which was excellent to the formation of a gaseous-phase contact fluorine of the halogenated hydrocarbon which used the hydrofluoric acid. Therefore, C1-C4 which contain one or more hydrogen atoms according to the method of this invention A fluorine-ized compound can be obtained. Moreover, there is little loss of the vanadium which is active species during the activation, and this catalyst is volatile vanadium (V). Generation of an oxy-fluoride or a fluoride is avoidable.

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## CLAIMS

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[Claim(s)]

[Claim 1] In the method of carrying out the gaseous-phase contact fluoridation of the halogenated hydrocarbon by the hydrofluoric acid, the mixed catalyst which makes chromium and a vanadium derivative a base material is used, and these two elements are mainly oxidation states III. Method characterized by being.

[Claim 2] Chromium and 90% or more of vanadium are an oxidation state III. The method according to claim 1 of existing.

[Claim 3] A V/Cr atomic ratio They are 0.1-3.5, and the method according to claim 1 or 2 which it is between 0.15-3 preferably.

[Claim 4] The method of any one publication of the claim 1-3 that a mixed Cr-V catalyst is a bulk catalyst.

[Claim 5] A bulk catalyst is chromium (III). And vanadium (III) Precipitate or gel of a compound It calcinates between 200 - 600 °C, or is chromium (III). And vanadium (III) The method according to claim 4 of being what is obtained by pyrolyzing an oxalate.

[Claim 6] The way according to claim 4 or 5 a bulk catalyst is what is prepared from vanadium chloride (III) and the sulfate of chromium, acetate, or a nitrate.

[Claim 7] The method of any one publication of the claim 1-3 that support adheres to chromium and the vanadium compound.

[Claim 8] The way according to claim 7 support is metallic oxides, such as 3 aluminum fluoride or an alumina, a magnesia, and a zirconia.

[Claim 9] A support catalyst is vanadium chloride (III) and chromium (III). The method according to claim 7 or 8 of being what is prepared from a chloride or a chromic-acid anhydride.

[Claim 10] 1-chloro - 2, 2, 2 - Application of the method by any one of the claims 1-9 to 1, 1 and 1 of triffe RUORO ethane, and fluorine-izing to 2-tetrafluoro ethane.

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